USEPA REGION 9 LABORATORY
RICHMOND, CALIFORNIA

STANDARD OPERATING PROCEDURE 353
LOW LEVEL VOLATILES

Revision 3
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1 SCOPE AND APPLICABILITY

This Standard Operating Procedure (SOP) describes the analysis of selected volatile organic compounds at low concentrations using gas chromatography/mass spectrometry (GC/MS) with selected ion monitoring (SIM) in aqueous samples. Samples with concentrations expected to exceed 500 ng/L should be analyzed by USEPA Region 9 Laboratory SOP 354 *Volatile Organic Compound Analysis in Water*. This SOP is based on procedures contained in EPA Method 524.2, Revision 4.1, 1995 as modified for low concentration analysis by the California Department of Health Services in *Determination of 1,2,3-Trichloropropane in Drinking Water by Purge and Trap Gas Chromatography/Mass Spectrometry*, February 2002. Deviations from Method 524.2 are described in Appendix A. Analytes and Quantitation Limits (QLs) are listed in Appendix B. Extension of the procedures to include additional VOCs must be arranged on a project basis.

The quality control (QC) criteria specified in this procedure do not meet compliance criteria for either drinking water or NPDES monitoring projects.

2 METHOD SUMMARY

Volatile organic compounds (VOCs) are purged from a 25-mL aqueous sample in a fritted sparge cell. The samples are fortified with internal standard (IS) and surrogate compounds (SURR) before they are purged. An inert gas (nitrogen) is bubbled through the sample in the sparge cell, which causes the purgeable VOCs to be transferred from the aqueous sample to the vapor phase. The vapor phase is swept through a trap containing an adsorbent material at ambient temperature where the VOCs are adsorbed. After the purging of the sample is completed, the adsorbent trap is heated and back flushed with helium which desorbs the VOCs onto a capillary column in a gas chromatograph (GC). The VOCs are separated in the GC column and detected by a mass spectrometer (MS).

Target VOCs are identified in the sample by comparing the characteristic ion(s) and GC retention time in the sample to the characteristic ion(s) and retention time of compounds in the standards analyzed under identical conditions. Each target and surrogate compound is quantitated by comparing the responses of the target and surrogate compound responses to the internal standard responses, using the average relative response factors from the most recent initial calibration.

3 DEFINITIONS

A list of terms and definitions specific to this procedure appears below. For terms and acronyms in general use at the USEPA Region 9 Laboratory refer to Appendix A of the Laboratory Quality Assurance Plan.

GC/MS Tuning Solution (MS tune): Bromofluorobenzene (BFB) used to evaluate the performance of the GC/MS system with respect to a defined set of method criteria.

FC43: Perfluorotributylamine. Compound used to tune the MS.

4 SAFETY & HEALTH

All laboratory operations must follow health and safety requirements outlined in current versions of the USEPA Region 9 Laboratory Chemical Hygiene Plan and the Region 9 Laboratory Business Plan. Potential hazards specific to this SOP as well as pollution prevention and waste management requirements are described in the following sections.

4.1 Chemical Hazards

Due to the unknown and potentially hazardous characteristics of samples, all sample handling and preparation should be performed in a well-vented laboratory fume hood.

The toxicity and carcinogenicity of each reagent used in this method may not be fully established. Each chemical should be regarded as a potential health hazard and exposure to them should be minimized by good laboratory practices. Refer to the Material Safety Data Sheets located in Room 118 (library) and the LAN at I:\MSDS IMAGES for additional information.

Some method analytes have been tentatively classified as known or suspected human or mammalian carcinogens. Stock standard solutions of these compounds must be prepared in a fume hood. Routine procedures in this SOP do not require contact with concentrated solutions or neat materials. All standard preparation procedures associated with this SOP should be performed in a fume hood wearing protective clothing (lab coats) and safety glasses.

Methanol is the primary solvent used for the preparation of standards in this procedure. Methanol is harmful if inhaled and may be fatal or cause blindness if ingested. Symptoms of overexposure via inhalation are drowsiness and intoxication, headache, visual disturbances leading to blindness, coughing and shortness of breath, collapse, and death at high concentrations. Skin contact may result in absorption producing toxic effects. Repeated skin contact may cause burning, itching, redness, blisters or dermatitis. Eye contact can cause burning, watering, redness and swelling. High vapor concentration will result in similar symptoms in the eyes. Medical attention must be sought whenever symptoms of inhalation or ingestion are observed as many effects are delayed due to the slow rate of metabolism.

Methanol is classified as a flammable solvent and must be handled accordingly. Use methanol in laboratory fume hood. The analyst must wear appropriate personal protective

equipment (laboratory coat, nitrile gloves and safety glasses). Store methanol in a flammables storage cabinet away from oxidizers and sources of ignition.

4.2 Equipment and Instruments

Follow the manufacturer's safety instructions whenever performing maintenance or troubleshooting work on equipment or instruments. Unplug the power supply before working on internal instrument components. Use of personal protective equipment may be warranted if physical or chemical hazards are present.

4.3 Pollution Prevention

Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operations. The USEPA Region 9 Laboratory places pollution prevention as the management option of first choice with regard to environmental management. Whenever feasible, laboratory personnel shall use pollution prevention techniques to address waste generation. When wastes cannot be feasibly reduced, recycling is the next best option. The *USEPA Region 9 Laboratory Environmental Management System* provides details regarding efforts to minimize waste.

Minimize waste through the judicious selection of volumes for reagents and standards to prevent the generation of waste due to expiration of excess materials. Reduce the volume of any reagent or standard described in Sections 7.2 or 7.3 so long as good laboratory practices are adhered to regarding the accuracy and precision of the glassware, syringes, and/or analytical balances used to prepare the solution. Reducing the concentration of a reagent is not allowed under this procedure because the impact of such a change on the chemistry of the procedure must be assessed prior to implementation.

Reduce the toxicity of waste by purchasing lower concentration stock standards, lower concentration stock reagents, and solutions to replace neat chemicals whenever possible. However, do not change the concentrations of standards and reagents specifically designated in this SOP

4.4 Waste Management

The USEPA Region 9 Laboratory complies with all applicable rules and regulations in the management of laboratory waste. The laboratory minimizes and controls all releases from hoods and bench operations. All analysts must collect and manage laboratory waste in a manner consistent with USEPA Region 9 Laboratory SOP 706 *Laboratory Waste Management Procedure*. Solid and hazardous wastes are disposed of in compliance with hazardous waste identification rules and land disposal restrictions. If additional guidance is needed for new waste streams or changes to existing waste streams, consult with EPA

Laboratory Safety, Health, and Environmental Manager (LaSHEM) or ESAT Health and Safety and Environmental Compliance Task Manager or designees.

This procedure generates the following waste streams:

Waste Stream Description	Waste Label	Hazard Properties
Laboratory solid waste (gloves, contaminated paper towels, disposable glassware, etc.)	Non-hazardous Waste	Not applicable
Aqueous acidic VOC waste (wastewater, hydrochloric acid, trace halogenated volatile compounds)	Hazardous Waste	Corrosive
Methanol waste (methanol, halogenated volatile compounds)	Hazardous Waste	Flammable, toxic
Waste pump oil (trace halogenated volatile compounds)	Hazardous Waste	Toxic

5 SAMPLE HANDLING AND PRESERVATION

5.1 Containers and Required Sample Volume

Samples must be received in pre-cleaned 40-mL VOA vials with Teflon-lined septa. No headspace or bubbles are acceptable. Three vials is adequate volume to complete the analysis and allow for reanalysis if required.

5.2 Internal Chain-of-Custody

Verify sample IDs and dates and times of collection against the chain-of-custody form.

Update the LIMS database internal custody form when sample containers are moved from the designated sample location. Change the container disposition to "active out" and the location to the appropriate room number. At the end of the day, return sample containers to the "Home" locations. Update the LIMS database using the "return to home location" feature and update container disposition to "available in". Verify that your initials are recorded whenever you update the LIMS custody information.

5.3 Preservation Verification

Samples should be preserved with hydrochloric acid to a pH of ≤ 2 at the time of sampling. The analyst must document unacceptable preservation in the work order memo field in LIMS and use the appropriate flag for data qualification (see Appendix R of the

USEPA Region 9 Laboratory Quality Assurance Plan). Preservation is not verified until sample analysis is complete.

5.4 Sample Storage

Samples must be stored at >0 and ≤ 6 °C in the refrigerators designated for sample storage in Rooms 201or 209. Retain samples for 60 days after the final analytical report is sent to the data user.

5.5 Holding Time

Samples must be analyzed within 14 days from collection. If samples were not preserved at the time of collection, analyze within 7 days of collection.

6 INTERFERENCES

6.1 Method interference may be caused by impurities in the purge gas, organic compounds out-gassing from the plumbing ahead of the trap, and solvent vapors in the laboratory. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running laboratory method and instrument blanks as described in Section 9.3.1. The use of non-polytetrafluoroethylene (PTFE) tubing, non-PTFE thread sealants, or flow controllers with rubber components in the purging device should be avoided.

6.2 Samples can be contaminated by diffusion of volatile organics through the septum seal into the sample during storage and handling.

6.3 Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the purging device and sampling syringe must be rinsed with reagent water between sample analyses. For samples containing large amounts of water-soluble materials, suspended solids, high-boiling compounds, or high purgeable levels, it may be necessary to wash out the purging device with a detergent solution between analyses, rinse it with distilled water, and then dry it in an oven at 105°C. The trap and other parts of the system are also subjected to contamination; therefore, frequent bake out and purging of the entire system may be required.

7 APPARATUS AND MATERIALS

This section describes recommended apparatus and materials to be used for the analysis. All equipment, reagents, standards, and supplies must meet the technical and QC requirements of the reference method. Substitutions may be made provided that they are documented and equivalency is maintained.

7.1 Instruments and Equipment

7.1.1 Gas Chromatograph (GC): Hewlett Packard/Agilent 6890 or 6890N, Agilent 7890A or, equivalent. The GC must be capable of multilevel temperature programming and constant carrier gas flow throughout the temperature range. The GC should be equipped with an automatic sample injector, split/splitless injection port, and Electronic Pressure Control (EPC).

7.1.2 Column: Hewlett Packard HP-624 25M x 0.20 mm, 1.12 micron film or equivalent. Any column capable of separating the target analytes and passing method QC without overloading at the concentration of the highest standard may be used.

7.1.3 Mass spectrometer: Hewlett Packard/Agilent 5973 or 5973N, Agilent 5975C, or equivalent, capable of scanning from 35 to 300 amu every two seconds or less using 70 volts (nominal) electron energy in the electron impact ionization mode. The MS must be able to produce a mass spectrum that meets acceptance criteria when 25 ng of BFB is injected through the GC inlet.

7.1.4 Data system: ChemStation (available from Agilent), or equivalent, able to control the GC/MS system and to acquire, store, and reduce mass spectral data. The software must be able to process any GC/MS data file by recognizing a GC peak within a retention time window and selectively scan specified masses (see Appendix B). The software must also allow integration of the ion abundance of any specific ion between specified times or scan number limits and to calculate the relative response factors (RRFs) and concentrations of analytes in samples.

7.1.5 Purge and Trap Concentrator: Tekmar 3000, Tekmar 3100, Teledyne Tekmar Stratum, OI Eclipse, or equivalent.

7.1.6 Autosampler: Varian Archon, OI Analytical Model 4552, or equivalent.

7.2 Reagents

Document the receipt of all reagents in the LIMS. A unique ID is assigned for each reagent. The reagent ID is reflected on all preparation and analysis batches.

7.2.1 Methanol (Purge & Trap grade).

7.2.2 Organic-free method blank water (prepared following USEPA Region 9 Laboratory SOP 205 *Preparation of Organic-free Method Blank Water*).

7.2.3 Hydrochloric acid, 6N HCl - Slowly add 50 mL of reagent grade concentrated HCl to 50 mL of organic-free method blank water. Prepare as needed. Also known as 1:1 or 1+1 HCl.

7.3 Standards

Document the receipt, preparation, and ampule open dates of all standards in the LIMS. Print and attach a LIMS standard label to all standard vials.

All ampulated calibration materials must be maintained in the refrigerator at >0°C to ≤6°C and protected from light. Use the manufacturer's expiration date for ampulated standards.

Open stock ampules and working standards must be maintained in a freezer at ≤-10 °C and protected from light. Open ampules are assigned an expiration date which is either six month from opening date, or the manufacturer expiration date, whichever is earlier. Working standards are assigned an expiration date which is either one month from preparation date, or the expiration date of the stock standard used in the preparation, whichever is earlier. Analysts must allow all standard solutions to equilibrate to room temperature before use. Replace standards sooner if analysis indicates that the solution has degraded. Dispose of any remaining solution in the correct waste container.

7.3.1 BFB, 5000 µg/mL: 4-Bromofluorobenzene VOA Tuning Compound solution, Restek catalog #30003 or equivalent.

7.3.2 1,2,3-Trichloropropane-d5 (TCP-d5): 2000 µg/mL, CPI catalog #Z020596-01, or equivalent.

7.3.3 1,2,3-Trichloropropane: 2000 µg/mL, Restek catalog #30429, or equivalent.

7.3.4 8011 Calibration Mix (EDB/DBCP): 2000 µg/mL, Restek catalog #30062, or equivalent

7.3.5 1,2-Dibromo-3-chloropropane (DBCP): 2000 µg/mL, Restek catalog #30270, or equivalent.

7.3.6 1,2,3-Trichloropropane: 200 µg/mL, Supelco catalog #48355, or equivalent.

7.3.7 Calibration Standards: EPA EDB/DBCP Mix: 2000 µg/mL, Supelco catalog #48225-U, or equivalent.

7.3.8 4-Bromofluorobenzene Tuning Solution (BFB Solution, 50 ng/µL): Add 1.5 mL of purge and trap grade methanol to a clean, dry, 2-mL volumetric flask using a gas tight syringe.

Add 20 µL of a BFB stock solution (5000 µg/mL) to the volumetric flask using a gas tight syringe with the syringe needle beneath the surface of the methanol.

Bring the volume up to 2 mL with purge and trap grade methanol. Cap the volumetric flask with its ground glass stopper and gently invert the flask three times to assure mixing (do not shake).

Pour the contents of the volumetric flask into a 2-mL screw cap vial equipped with a Teflon-lined screw cap and a Mininert valve. (Do not use pipettes to transfer VOA solutions because the vacuum used to draw the solutions up into the pipettes can cause some volatile compounds to come out of solution).

7.3.9 Internal standard and surrogate solution (TCP_ISSUR 1.25 µg/mL)

Add 8 mL of purge and trap grade methanol to a clean, dry, 10-mL volumetric flask.

Add the stock standard solutions in the amounts indicated in the table below to the volumetric flask using a gas tight syringe with the syringe needle beneath the surface of the methanol. Rinse the syringe 5 times with methanol and a small amount of the next stock standard to be dispensed between sampling different mixtures.

Bring the volume up to 10 mL with purge and trap grade methanol. Cap the volumetric flask with its ground glass stopper and gently invert the flask three times to assure mixing (do not shake).

Stock Standards	Supplier	Stock Conc., µg/mL	Amount, µL	Final Volume, mL	Final Conc. µg/mL
TCP-d5	Restek	2000	6.25	10	1.25
BFB	Restek	5000	2.5	10	1.25

Pour the contents of the volumetric flask into a clean 5-mL standard reservoir vial and immediately install the standard reservoir in the appropriate standard position on the autosampler. Print and attach a LIMS standard label to the standard vial or the back panel of the autosampler adjacent to the vial.

7.3.10 Calibration mix (5/10 µg/mL)

Add 1.5 mL of purge and trap grade methanol to a clean and dry 2-mL volumetric flask using a 5 mL syringe.

Add the stock standards to the volumetric flask using a gas tight syringe with the syringe needle beneath the surface of the methanol in the amounts indicated in the table below. Rinse the syringe 5 times with methanol and a small amount of the next stock standard to be dispensed between sampling different mixes.

Stock Standards	Supplier	Stock Conc., µg/mL	Amount, µL	Final Volume, mL	Final Conc. µg/mL
8011 Cal Mix EDB/DBCP	Restek	2000	5	2	5*
1,2,3-Trichloropropane	Restek	2000	5	2	5
DBCP	Restek	2000	5	2	5*

*DBCP concentration is 10 µg/mL in the calibration mix as a total from two sources.

Bring the volume up to 2 mL with purge and trap grade methanol. Cap the volumetric flask with its ground glass stopper and gently invert the flask three times to assure mixing (do not shake).

Transfer the contents of the volumetric flask into a 2-mL screw cap vial equipped with a Teflon-lined screw cap and a Mininert valve by gently pouring the solution out of the volumetric flask and into the vial.

7.3.11 Calibration mix (0.25/0.50 µg/mL)

Add 1.5 mL of purge and trap grade methanol to a clean and dry 2-mL volumetric flask using a gas tight syringe.

Add 0.1 mL of the 5 µg/mL Calibration mix to the volumetric flask using a gas tight syringe with the syringe needle beneath the surface of the methanol.
Bring the volume up to 2 mL with purge and trap grade methanol. Cap the volumetric flask with its ground glass stopper and gently invert the flask three times to assure mixing (do not shake).

Transfer the contents of the volumetric flask into a 2-mL screw cap vial equipped with a Teflon-lined screw cap and a Mininert valve by gently pouring the solution out of the volumetric flask and into the vial.

7.3.12 Second Source Verification (SCV) solution (EDB/DBCP//TCP_SCV-1 µg/mL)

Add 4 mL of purge and trap grade methanol to a clean and dry 5-mL volumetric flask using a gas tight syringe.

Add the stock standards to the volumetric flask using a gas tight syringe with the syringe needle beneath the surface of the methanol in the amounts indicated in the table below. Rinse the syringe 5 times with methanol and a small amount of the next stock standard to be dispensed between sampling different mixes.

Stock Standards	Supplier	Stock Conc., µg/mL	Amount, µL	Final Volume, mL	Final Conc. ug/mL
EPA EDB/DBCP Mix	Supelco	2000	2.5	5	1
1,2,3-Trichloropropane	Supelco	200	25	5	1

Bring the volume up to 5 mL with purge and trap grade methanol. Cap the volumetric flask with its ground glass stopper and gently invert the flask three times to assure mixing (do not shake).

Transfer the contents of the volumetric flask into a 5-mL screw cap vial equipped with a Teflon-lined screw cap and a Mininert valve by gently pouring the solution out of the volumetric flask and into the vial.

7.4 Supplies

7.4.1 Gas-tight syringes (5-µL, 10-µL, 25-µL, 50-µL, 100-µL, 250-µL, 500-µL, 1-mL, 5-mL, 10-mL, 25-mL and 50 mL).

7.4.2 25-mL fritted sparge vessels.

7.4.3 Disposable Pasteur pipettes.

7.4.4 pH paper (pH 0-14 range).

7.4.5 Trap K (VOCARB 3000, or equivalent).

7.4.6 40-mL VOC vials for standards with screw-hollow cap lined with 22 mm PTFE-faced silicone septa.

8 ANALYTICAL PROCEDURES

8.1 Instrument Operation

Set-up the GC/MS following operating instructions provided by the manufacturer. Use operating parameters provided in Appendix E as a starting point. Parameters for the autosampler and concentrator are found in Appendix D.

Check the mass spectrometer for leaks on a daily basis, prior to the analysis of the tuning compound. Refer to Section 8.4.1 and Appendix F for system maintenance requirements.

Ensure that waste containers are properly connected and labeled and have sufficient empty volume for the waste that will be generated during instrument operation.

8.1.1 Mass calibration

Mass calibration of the analytical system must be performed prior to an initial calibration, whenever the source is cleaned, or whenever there is a mass miss-assignment is noted. Mass calibration is performed to ensure the accurate assignment of masses to ions (Appendix E). Use perfluorotributylamine (FC43) to perform mass calibration of the instrument.

Refer to Section 9.2.1 and Appendix C for frequency, acceptance criteria, and corrective action requirements.

8.1.2 GC/MS tuning

The GC/MS system must meet the mass spectral ion abundance criteria for BFB prior to at the beginning of each analytical period. Proper tuning of the instrument is necessary to produce standardized fragmentation patterns of target compounds.

Inject or purge 0.5 µL of the BFB solution using the operating parameters provided in Appendix D.

The autofind procedure will automatically find the BFB peak, average three scans (the peak apex scan and the scans immediately preceding and following the apex), perform a background subtraction and print out a hard copy of the spectrum, the chromatogram, and the table of ion abundances.

Refer to Section 9.2.2 and Appendix C for frequency, acceptance criteria, and corrective action requirements.

8.2 Calibration and Standardization

8.2.1 Initial Calibration

Prior to analyzing an initial calibration, ensure that proper system maintenance and GC/MS tuning (auto-tune and/or manual tune) has been performed (refer to Appendices E and F).

Perform an initial calibration using six calibration standards. The recommended concentrations are listed in the following table.

Analysis Type	Calibration Levels					
	1 (CRL)	2	3	4 (CCV)	5	6
EDB/DBCP/TCP*, ng/L	5	10	25	50	100	500
Standard Amounts (µL) for each calibration level added to 50 mL Acidified Water						
Calibration mix 0.25/0.50 µg/mL	1	2	5	10		
Calibration mix 5.0/10 µg/mL					1	5
1.0 µg/mL SCV Standard				2.5		

*DBCP concentrations are twice the listed concentrations.

Update the initial calibration response factors for the method by associating the current data file with each calibration level and save the method.

Print the raw area report for an internal standard or the target analyte for single analyte analysis. From the ChemStation menu, select initial calibration → edit compound → view → page 3. Verify that the method was updated correctly. Print analyte list from the ChemStation menu by selecting initial calibration → list compound, to verify that the average response factor is used.

Analyze an SCV standard at calibration level 4 to verify the accuracy of the calibration materials and preparation used in the initial calibration.

Initially, before processing any samples, the analyst should demonstrate that all parts of the equipment in contact with the sample and reagents are interference-free. This is accomplished through the analysis of a method blank or an instrument blank.

Refer to Section 9.2.3 and Appendix C for frequency, acceptance criteria, and corrective action requirements.

8.2.2 Continuing Calibration

Prior to analyzing a continuing calibration, ensure that proper system maintenance and GC/MS tuning (mass axis calibration) has been performed (Appendices E and F).

8.2.2.1 Continuing Calibration Verification (may also serve as the LCS)

Analyze a calibration verification standard following the BFB tune check.

Refer to Section 9.2.4 and Appendix C for frequency, acceptance criteria, and corrective action requirements.

Note that CCV and LCS/BS are the same and that one analysis can serve both functions (i.e. instrument calibration verification and batch accuracy QC).

8.2.2.2 Quantitation Limit Verification Standard (CRL)

Analyze a CRL standard at the reporting limit (the concentration of the lowest point of the initial calibration).

Refer to Section 9.2.5 and Appendix C for frequency, acceptance criteria, and corrective action requirements.

8.3 Analysis

8.3.1 Sample Preparation

Allow the sample to reach ambient temperature before analysis.

Check that the numbers on the vials coincide with the numbers on the LIMS batch to ensure that the correct sample is being analyzed.

Note if the sample has an unusual color or other physical properties. If any physical signs of contamination are present, screen the samples to protect the analytical system from damage or contamination, and to determine the appropriate subsequent dilutions. Record unusual items in the LIMS "MMO" field.

8.3.2 Sample Analysis and Analytical Sequence

This section describes setting up the analytical sequence and performing the instrumental analysis. Record the analytical sequence in the instrument run log and the LIMS sequence page.

Prepare instrument and batch QC samples in acidified organic-free method blank water.

Prepare the samples to be analyzed. The following table represents the spike levels recommended for most projects:

Spike Amounts, Autosampler, 25 mL Purge

Sample	TCP_ISSUR Mix 1.25 µg/mL, µL	Calibration Mix 0.25/0.50 µg/mL, µL
Blanks	1.0	NA
Samples	1.0	NA
BS/LCS*	1.0	10.0
MS/MSD#	1.0	8.0

* Prepare 50 mL and transfer to 40-mL vial. Also the CCV.
# 40-mL Sample vial spiked with Calibration Mix
NA = Not Applicable

Load the samples in the autosampler according to their designated positions in the sequence file. The recommended analysis sequence is:

1. BFB
2. CCV/LCS
3. CRL (QLS)
4. Method Blank
5. Samples, sample dilutions, and/or QC samples as needed.
6. Instrument blanks, as needed

Enter sample sequence in the instrument software. Include the laboratory sample number (work order-sample number) in the "Sample" field and dilution level, if any in the "Multiplier" field.

Name the data files according to the data file naming convention outlined in Appendix G.

Program the autosampler to use the appropriate locations for the analysis.

8.3.3 Analyte Identification and Quantitation

8.3.3.1 Analyte Identification

In order for a target compound to be identified as present in a sample both the retention time and the characteristic ions of the peak must match those of the standard.

For relative retention time, the peak must elute within 0.06 relative retention time units of the analyte in the continuing calibration standard. The relative retention time is the retention time of the target divided by the retention time of the associated IS. If the relative retention time for the target analyte in the CCAL is 0.82 then the peak in the sample must have a relative retention time of 0.76 to 0.88.

The relative intensities of the characteristic ions must agree within 20% between the standard and sample spectra.

If a compound cannot be verified using these criteria but in the technical judgment of the analyst is present, report the analyte and include supporting evidence in the raw data package.

Cross out all reported hits that do not meet qualitative criteria. Date and initial the change.

Review the chromatogram for possible false negatives and edit results as needed.

8.3.3.2 Analyte Quantitation

Quantitate the data and print out quantitation reports and chromatograms. Use the average relative response factor from the initial calibration for quantitation.

Calculate results for target analytes using the following equation:

Conc. (ng/L) = Ax * AMTIS * DF / (AIS * RRF)

Where:

Ax	=	area of the characteristic ion of the compound
AMTIS	=	amount of internal standard in ng/L (200 ng/L)
DF	=	dilution factor
AIS	=	area of the characteristic ion of the associated internal standard
RRF	=	analyte average relative response factor from the initial calibration

8.3.3.3 Manual Integration

Where the chromatography software integrates the signal inconsistently, follow USEPA Region 9 Laboratory SOP 835, *Chromatographic Integration Procedures*. All manual chromatographic integration must be initialed and dated by the analyst and approved by the supervisor, Chemistry Technical Director, Quality Assurance Officer, or designees.

8.3.4 QC Review

8.3.4.1 Process and review the results for the IB/MB, CCV/LCS/BS, and CRL, samples and QC samples (MS/MSD). Print a ChemStation Evaluate Continuing Calibration Report using the appropriate settings to verify that the CCV and CRL (QLS) QC sample results are within QC limits. See Section 9.2 for instrument QC requirements; see Section 9.3 for Batch QC requirements.

8.3.4.2 Determine if surrogate recoveries for field and QC samples are within QC limits. See Section 9.4 for Sample QC requirements.

8.3.4.3 Review all sample results:

8.3.4.3.1 Determine if any samples contain target analytes at concentrations exceeding the calibration range. If so, determine if dilution is required, or if the analyte will be quantitated using the full scan procedures (EPA Region 9 Laboratory SOP 354).

8.3.4.3.2 Review the chromatogram for possible false negatives.

8.3.4.3.3 Manually cross out all compounds that do not meet the qualitative criteria and document the reason on the quantitation report.

8.3.4.3.4 If a run is rejected for any reason, mark the raw data "Not Used" in large print and document the reason on the quantitation report.

8.3.4.4 Qualify and flag results in the LIMS Data Entry/Review table following Appendix R of the USEPA Region 9 Laboratory Quality Assurance Plan.

8.3.5 Data Export and LIMS Entry

Export data from the instrument into text files. Import into the LIMS using DataTool. Review final results in the LIMS.

Report all results to two significant figures. Report detected results to one-half the QL. Flag values between one-half the QL and the QL as estimated (J) and provide the C1 qualifier.

8.4 Maintenance

The analyst should observe trends in the data such as declining response, erratic relative response, loss of classes of compounds, etc., which may signal the need for instrument maintenance. Document all routine maintenance or corrective actions taken in the maintenance logbook.

The following sections describe possible causes and corrective actions for common problems for GC and MS operations. Refer to Appendix E for routine preventative maintenance procedures and schedule.

8.4.1 GC Maintenance

Symptoms of common problems:

- Carryover
  Possible causes: Analyzing a sample containing high molecular weight components or analyzing high-level and low-level samples sequentially.
  Corrective action: As necessary, replace inlet liner, clean inlet, bake out inlet, bake out column, clip column, replace septum, replace column.

- Shorter retention time.
  Possible cause: column flow rate problem.
  Corrective action: check flow rate and adjust as necessary.

- Longer retention time and or smaller peaks.
  Possible causes: column flow rate problem, injection port leak, or column contamination.
  Corrective action: As necessary, check for leaks, replace septum, replace the liner, replace the lower injection port seal, and cut the column (a few inches to a foot or more) from the injector end. If issues remain, replace the column.

- Loss of resolution.
  Possible causes: column flow rate problem, injection port leak, or column contamination.
  Corrective action: Check for leaks, replace septum, liner, and inlet seal, clip the column (a few inches to a foot or more) from the injector end. If issues remain, replace the column.

8.4.2 MS maintenance:

Trend to be observed:

- Low m/z 502 to 69 ratio

- Failing tune checks

Resolution: Clean the source.

9 QUALITY CONTROL

The USEPA Region 9 Laboratory operates a formal quality control program. As it relates to this SOP, the QC program consists of a demonstration of capability, and the periodic analysis of MB, LCS, and other laboratory solutions as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of the data that are generated. A summary of QC criteria is provided in Appendix C.

9.1 Demonstration of Capability

A Demonstration of Capability must be in place prior to using an analytical procedure and repeated if there is a change in instrument type, personnel, or method. Follow procedures described in USEPA Region 9 Laboratory SOP 880 *Demonstration of Capability* for more details.

9.2 Instrument QC

9.2.1 Mass calibration

Review the FC43 spectrum for compliance with the criteria list in Appendix C.

If the FC43 spectrum does not meet the criteria, corrective action must be taken. The corrective action may be as simple as adjusting the voltages/retuning the MS. If retuning the MS does not produce adequate FC43 spectra, further maintenance such as cleaning the ion source may be required.

9.2.2 GC/MS Tune

Review the BFB spectrum for compliance with the criteria list in Appendix C.

If the ion abundances, degradation, or tailing fail to meet the criteria, the BFB chromatogram should be examined for any obvious chromatographic problems (e.g., bad injection leading to poor response etc.). If the problem is related to poor chromatography, take the necessary corrective action and reanalyze the BFB. If the BFB continues to fail the ion abundance criteria, retune the mass spectrometer. It may also be necessary to clean the ion source or take other corrective action to achieve the ion abundance criteria.

Reanalyze samples injected after the 12-hour time period has elapsed.

9.2.3 Initial Calibration

Each GC/MS system must be calibrated whenever corrective action is performed which may change instrument response (e.g., ion source cleaning, column replacement, etc.) or if the continuing calibration acceptance criteria cannot be met.

No quantitation ion may saturate the detector.

The data system calculates the relative response factor (RRF) for each target compound and surrogate compound using the following equation:

$$RRF = (Ax)(Cis) / (Ais)(Cx)$$

Where

Ax = Area of quantitation ion of compound x. The quantitation ions and internal standard assignments are listed in Appendix B.
Ais = Area of quantitation ion for associated internal standard
Cx = Concentration of compound x
Cis = Concentration of the associated internal standard

The data system calculates the average RRF (RRFavg) for all analytes.

The data system calculates the percent relative standard deviation (%RSD) of the RRF values for each compound using the following equation.

$$\%RSD = (SD/ RRF_{avg})*100$$

Where

$$SD = \sqrt{\frac{\sum_{i=1}^{n}(x_i - x_{ave})^2}{n-1}}$$

The %RSD and SCV accuracy requirements are listed in Appendix C.

If an ICAL fails because of one standard, a fresh solution of that standard may be reanalyzed and substituted for the standard that failed in the ICAL. If the failure is repeated (or the problem is not isolated to one calibration point), the system must be repaired so that the criteria are satisfied before any samples are analyzed.

If SCV criteria (see Appendix C) are not met, the SCV must be reanalyzed. If it fails again, prepare a fresh solution. If failure persists, take corrective action as needed, including reanalysis or re-preparation and reanalysis of the initial calibration, if necessary.

9.2.4 Continuing Calibration Verification (may also be evaluated as the LCS)

Examine the areas of the quantitation ions of the internal standards in the calibration verification standard. If the area for any internal standard changes by more than 50% from the internal standard areas of the continuing calibration level of the most recent initial calibration, the CCV may be reanalyzed. If the failure is repeated, the analysis shall be terminated, the problem corrected, and a new calibration curve prepared.

Examine the retention times of internal standards in the calibration verification standard. If the retention time for any internal standard changes by more than 0.5 minutes compared to the continuing calibration level of the most recent initial calibration sequence, inspect the chromatographic system for malfunctions and take corrective action as needed and prepare a new calibration curve.

The data system calculates the percent deviation (%D) of the RRF values for each compound using the following equation:

$$\%D = \frac{RRF_c - RRF_{avg}}{RRF_{avg}} x\ 100$$

Where:

RRF_c	=	Relative Response Factor of compound c.
RRF_{avg}	=	Average Relative Response Factor.

If the continuing calibration does not meet %D criterion listed in Appendix C, the analysis shall be terminated, the problem corrected, and a new continuing calibration analyzed.

Qualify and flag results as needed in the LIMS Data Entry/Review table following Appendix R of the Region 9 Quality Assurance Manual.

9.2.5 Quantitation Limit Standard (CRL or QLS)

CRL must be analyzed at the beginning of the analytical run, typically just after the CCV. The concentrations match the QL concentration (at the instrument). The recovery of analytes in the CRL is calculated as:

$$\%R = \frac{M}{T} \times 100$$

Where

%R	=	percent recovery of the standard.
M	=	measured concentration of the analyte, ng/L.
T	=	true concentration of the analyte in the ng/L.

Check that the recoveries meet the criteria specified in Appendix C.

If the CRL recovery does not meet criteria provided in Appendix C, rerun the CRL once to verify. If still unacceptable determine the cause, take corrective action.

Qualify and flag results as needed in the LIMS Data Entry/Review table following Appendix R of the Region 9 Laboratory Quality Assurance Plan.

9.3 Batch QC

9.3.1 Method Blank (equivalent to an instrument blank in this procedure)

- Analyze a method blank (MB) to demonstrate that the entire analytical system is free of contamination.

- Evaluate the MB as soon as possible after it has been analyzed to determine if the results are within QC limits. See Appendix C for QC limits.

- Corrective action - If the MB result exceeds QC limits, check the associated samples as follow:

  1. If the sample result is less than five times the MB result, reanalyze the MB. If the MB result still exceeds QC limits, qualify the data as described in the Region 9 Lab QA Plan, Appendix R for each analyte found in the MB.
  2. If the sample result is greater than five times the MB result or is not detected, report the sample result.

- If the surrogate recovery does not meet acceptance criteria, reanalyze the MB. If the surrogate recovery still does not meet acceptance criteria, the batch should be reanalyzed.

9.3.2 Laboratory Control Sample (equivalent to the CCV in this procedure – one analysis serves both functions)

- Analyze a laboratory control sample (LCS) to demonstrate that the analytical system is in control. An LCS is analyzed once per batch or every 20 samples, whichever is more frequent. The LCS is an MB spiked with matrix spiking solution.

- Calculate the percent recovery (%R) using the following equation:

$$\%\ R = [(SSR - SR)/SA] \times 100$$

Where,
SSR = Spiked sample result
SR = Unspiked sample result
SA = Spike added

- The %R must be within the QC limits in Appendix C. If acceptable recoveries cannot be achieved, reanalyze the LCS. If the LCS result still exceeds QC limits, correct the error (which may include maintenance or repair and recalibration of the instrument) and reanalyze the LCS and all associated samples.

9.3.3 Matrix Spike/Matrix Spike Duplicate

- Matrix spike (MS) and matrix spike duplicate (MSD) samples are analyzed for each batch of twenty or fewer samples analyzed as a group.

- Calculate the recovery of each analyte.

- Calculate the relative percent differences (RPD) of the recoveries of each analyte in the MS and MSD using the following equation:

$$RPD = \frac{(MSC - MSDC)}{(MSC + MSDC)/2} \times 100$$

Where,
MSC = Measured concentration of analyte in MS
MSDC = Measured concentration of analyte in MSD

- See Appendix C for QC limits.

  The MS/MSD recovery limits are advisory limits only. If the limits are not met, then no further action is required, as long as the LCS is within limits, since the purpose of these analyses is to determine matrix effects on compound recovery. However, frequent failure to meet the recovery or RPD criteria should alert the analyst that a problem may exist and must be investigated. The analyst should analyze the matrix spike solution and check the recoveries of the spike compounds. A new solution should be prepared if the recoveries are not within 20% of expected.

- The table below lists the action to be taken based on the LCS and MS/MSD results.

QC ACCEPTANCE MATRIX + = PASS – = FAIL								
CASE	1	2	3	4	5	6	7	8
LCS - % REC	+	+	+	+	–	–	–	–
MS/MSD -% REC	+	–	+	–	+	–	+	–
MS/MSD – RPD	+	+	–	–	+	+	–	–

Case 1: Analysis batch acceptable.
Case 2: Analysis batch acceptable; matrix effect confirmed.
Cases 3 & 4: Analysis batch is unsatisfactory. Investigate MS/MSD problem and document findings in the LIMS memo field.
Cases 5, 6, 7, & 8: Analysis batch rejected. If additional sample volume is available, the batch should be reanalyzed.

9.4 Sample QC

9.4.1 Surrogate Recovery

Calculate the surrogate recovery in all field and QC samples immediately after analysis using the following formula:

$$\%R = (\text{Amount Found}/\text{Amount Spiked}) \times 100.$$

Take the following steps if surrogate recovery is not within the limits:

1. Ensure that there are no calculation errors, and check the system performance.

2. Reanalyze the sample if a system performance problem or calculation error is not evident. The sample may be diluted for reanalysis if examination of the chromatogram so indicates.

Do not reanalyze undiluted samples with surrogate recoveries outside the limits if the diluted analysis with acceptable surrogate recoveries is being submitted. Report the event in the run log.

Do not reanalyze the MS/MSD samples, even if surrogate recoveries are outside the limits.

If the sample associated with the MS/MSD analyses does not meet the surrogate recovery criteria, it should be reanalyzed only if the matrix spike and duplicate surrogate recoveries are within the limits. If the sample and spikes show the same pattern (i.e., outside the limits), then the sample does not need reanalysis.
If the surrogate recoveries of the reanalysis are within limits, then the problem was within the laboratory's control. Report the results from the reanalysis and submit the data from both analyses. The problem must be documented in the LIMS MMO field.

- If the reanalysis does not solve the problem and additional sample volume is available, the failing samples should be re-analyzed.

- If sample re-analyses is unfeasible, or surrogate recoveries of the re-analyses are also outside the QC limits, report the results from the first analysis and submit the data from both analyses. Distinguish between the original analysis and the re-analysis by adding the "RE" suffix to the sample ID in the re-analysis. The problem must be documented in the LIMS MMO field.

9.4.2 Internal Standard Area:

- Evaluate the internal standard areas in all field and QC samples immediately after analysis.

The internal standard areas must be within QC limits outlined in Appendix C.
Take the following steps if the internal standard areas are not within the limits:

1. Check the system performance.

2. Re-analyze the sample if a system performance problem is not evident. The sample may be diluted for re-analysis if examination of the chromatogram so indicates.

Do not reanalyze undiluted samples with internal standard areas outside the limits if the diluted analysis with acceptable internal standard areas is being submitted.

Do not reanalyze the MS/MSD samples, even if internal standard areas are outside the limits.

If the sample associated with the MS/MSD analyses does not meet the internal standard areas criteria, it should be reanalyzed only if the matrix spike and duplicate internal standard areas are within the limits. If the sample and spikes show the same pattern (i.e., outside the limits), then the sample does not need reanalysis.
If the internal standard areas of the reanalysis are within limits, then, the problem was within the laboratory's control. Report the results from the reanalysis and submit the data from both analyses. Distinguish between the analysis and reanalysis by adding an "RE" suffix to the sample ID on the reanalysis. The problem must be documented in the LIMS MMO field.

9.5 Method Performance

The following table summarizes method performance from LCS data (water matrix) for the period March 1, 2016 to August 30, 2016.

Method Performance

Analyte	Number of Measurements	Mean Recovery, %	95% Confidence Interval (2σ)
1,2,3-Trichloropropane	41	104	91.2-116
1,2-Dibromoethane	41	107	92.4-121
1,2-Dibromo-3-chloropropane	41	87.5	63.7-111

Functional areas of the SOP that may be significant sources of analytical error are:

1. Addition of internal standard: The amount and concentration of internal standard

added is critical. The nominal concentration is used in calculating target analyte concentration.

2. Samples must be stored as outlined in the SOP to minimize analyte degradation and solvent evaporation.

3. Sample temperature: Samples must be allowed to come up to room temperature prior to analysis. Failure to do so will cause heavy molecular weight analytes to precipitate thus reducing the observed concentration.

4. Poor column condition may results in inadequate analyte separation and inaccurate integration.

10 DOCUMENTATION

10.1 Standards

All standards (ICAL, ICV/CCV, QL, MS/MSD, and LCS) are recorded in the LIMS. A copy of each Analytical Standard Record associated with sample analysis is included in the data package, if required.

10.2 Reagents

Record all reagents used for each analytical batch in the LIMS.

10.3 Analytical sequence

The analytical sequence is documented in the LIMS or in the instrument Run Log. Case Number, SDG number, date of analysis, QC solution IDs, analyst initials, lab sample IDs, client sample IDs, dilution factors and comments, if any, are recorded.

10.4 Analytical Report and Data Package

Analytical reports are produced using the LIMS. The data package is produced from LIMS and manual log records.

10.5 Maintenance Logbook

Maintain a maintenance logbook for each instrument covered in this SOP. Document the following:

- Initial installation and performance
- Subsequent instrument modifications and upgrades, including major software upgrades

- All preventive or routine maintenance performed including repairs and corrective or remedial actions. Whenever corrective action is taken, record the date, the problem and resolution, and documentation of return to control.

All entries should be made in accordance with USEPA Region 9 Laboratory SOP 840, *Notebook Documentation and Control*.

10.6 SOP Distribution and Acknowledgement

Distribute the approved SOP to all laboratory staff expected to perform the SOP or review data generated by the SOP. The Lab QC Database is used to maintain the list of assigned analysts for each SOP. Analyst training is documented via the Training Record form and the Read and Understood Signature log; the latter is entered into the Lab QC Database.

10.7 SOP Revisions

Revisions to this SOP are summarized in Appendix H.

11 REFERENCES

EPA Region 9 Laboratory documents (SOPs, the Laboratory Quality Assurance Plan, etc.) are not included in this list. Analysts are referred to the SOP database on the local area network, LIMS, or the Lab QA SharePoint site for these documents; laboratory users should contact the Chemistry Team Leader or Laboratory QAO for copies of any supporting documents.

Agilent Technologies EnviroQuant ChemStation User's Guide.

Agilent Technologies/HP 5975C GC/MS User's Manual.

California Department of Health Services, Division of Drinking Water and Environmental Management, Sanitation and Radiation Laboratories Branch, Berkeley, CA 94704; *Determination of 1,2,3-Trichloropropane in Drinking Water by Purge and Trap Gas Chromatography/Mass Spectrometry,* February 2002.

OI Analytical Model 4552 Autosampler User's Manual.

Teledyne Tekmar Stratum Purge & Trap User Manual.

USEPA Method 524.2, *Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry* Revision 4.1, 1995.

APPENDIX A.
DEVIATIONS FROM THE REFERENCE METHOD

1. This SOP, following the Region 9 QA Plan, specifies preservation and storage temperatures of > 0° to ≤ 6°C, while the reference method specifies < 4°C.

2. Method 524.2 describes using the spectra generated by the analytical system as reference spectra for target analyte identification. This SOP specifies the use of selected ion monitoring (SIM) which relies on the presence of specific ions at the retention time of the standard. A full spectrum is not available for comparison, but lower detection limits are obtained.

3. Method 524.2 uses fluorobenzene as the internal standard; this procedures follows recommendations in the California Department of Health Services method and uses deuterated 1,2,3-trichloropropane.

4. Method 524.2 indicates that "The GC retention time of the sample component should be within three standard deviations of the mean retention time of the compound in the calibration mixture." The retention time window of ± 0.2 min used in this procedure prevents false negatives due to retention time shifts that may result from instrument changes or chromatographic anomalies caused by sample matrix. All peaks identified by the data system are reviewed by the analyst to confirm qualification.

Note: the California Department of Health Services method for 1,2,3-trichloropropane uses a heated purge; this procedures does not heat the sample while purging.

APPENDIX B.
ANALYTES AND QUANTITATION LIMITS

The following table provides the target analytes list for this SOP with the CAS number and quantitation limits.

Analyte	Chemical Abstracts Registry Number (CASRN)	Water Quantitation Limit, ng/L
1,2,3-Trichloropropane	96-18-4	5
1,2-Dibromoethane	106-93-4	5
1,2-Dibromo-3-chloropropane	96-12-8	10

SIM Ions, System Monitoring Compounds, and Internal Standards

Compound Name	IS	SMC Reference	SIM Primary Ion, m/z	SIM Secondary Ion m/z
1,2-Dibromoethane	TCP-d5	BFB	107	109
1,2,3-Trichloropropane	TCP-d5	BFB	75	61, 110
1,2-Dibromo-3-chloropropane	TCP-d5	BFB	157	75, 155
Bromofluorobenzene (BFB)	TCP-d5	-----	95	174, 176
1,2,3-Trichloropropane -d5 (TCP-d5)	-----	-----	79	114

APPENDIX C.
QUALITY CONTROL MEASURES AND CRITERIA

Parameter	Frequency	Criteria
BFB	Every 12 hrs.	See below
IC %RSD	As needed	≤ 20%
SCV %D	As part of IC	≤ 30%
CCV %D	Every 12 hrs.	≤ 30%
CCV IS/SURR Area	Every 12 hrs.	±30% of IC
CCV Ret Time Drift	Every 12 hrs.	±30 sec of IC
LCS Recovery*	Every 12 hrs.	
1,2,3-Trichloropropane	85-123 %	
1,2-Dibromoethane	85-128 %	
1,2-Dibromo-3-chloropropane	52-123 %	
QLS Recovery	Every 12 hrs.	60 – 140%
MB, SB	Every 12 hrs.	< ½ QL
MS/MSD*	Each Batch of 20 samples or less	
1,2,3-Trichloropropane	51-147 % Recovery	≤ 20 RPD
1,2-Dibromoethane	65-133 % Recovery	≤ 34 RPD
1,2-Dibromo-3-chloropropane	23-171 % Recovery	≤ 30 RPD
Surrogate Recovery	Each Sample	80-119%
Sample IS Area	Each Sample	±30% of CCV1

* Limits calculated from historical data from March 01, 2016 to August 31, 2016.

BFB ion abundance ratios must meet the following criteria:

Mass (m/z)	Relative Ion Abundance Criteria
50	15 - 40 % of mass 95
75	30 - 60 % of mass 95
95	Base peak, 100 % relative abundance
96	5 - 9 % of mass 95
173	< 2 % of mass 174
174	>50 % of mass 95 (Mass 95 must be base peak)
175	5 - 9 % of mass 174
176	> 95 but < 101 % of mass 174
177	5 - 9 % of mass 176

The Agilent ChemStation software requires that the FC43 spectrum meet the following criteria:

Mass	Target % of Mass 69
50	0.3-5
69	100
131	20-120
219	20-120
414	0.3-10
502	0.3-10

APPENDIX D.
INSTRUMENT INFORMATION

PURGE & TRAP CONCENTRATOR/AUTOSAMPLER PARAMETERS

Recommended Purge and Trap Concentrator Operating Parameters

The operating parameters for the purge & trap concentrators. These parameters may vary slightly to optimize instrument responses.

PARAMETER	SETTING
Standby temperature	35°C
Preheat temperature	N/A
Prepurge time	0.5 min
Sample temperature	Ambient
Purge Time	11 minutes
Dry purge	2 minutes
Dry purge flow	100 mL/min
Purge Flow	40 mL/min
Desorb preheat temperature	245°C
Desorb	2.00 minutes @ 250°C
Desorb flow	150 mL/min
Bake	15 minutes @ 260°C
Auto drain	Off (controlled by Autosampler)
Bake gas bypass	Off
Valve temperature	150°C
Mount temperature	100°C
Line temperature	150°C

OI Analytical Model 4552 Autosampler or Varian Archon

The Autosampler delivers an aliquot of the water sample directly from the 40 mL sample vial into the sparge vessel on the concentrator. The Autosampler can be programmed to add the internal standard and surrogate into the sample during the transfer process. In water analysis mode, the settings for the Autosampler method are equivalent to the settings on the concentrator. The following parameters must be established on the Autosampler: sample volume, dilution, standard addition, purge time (same as concentrator), and number of vials to be analyzed.

Standards loading:

1. Prepare standards and blank spikes in a 50-mL volumetric flask with acidified method blank water.
2. Gently invert three times.
3. Gently pour the standard solution into the 40-mL vial (pre-label with information about the standard), down the side of the vial, without any agitation. Overfill the vial to form an inverted meniscus. Cap the vial. Invert the vial to ensure that there

are no air bubbles present.

4. Gently place the vial in the appropriate autosampler position.
5. The autosampler will analyze a 25 mL aliquot and add 1 µL of the 5 µg/mL VOA IS solution. The amount used results in the analytical equivalent of 200 ng/L.

Sample Loading:

1 Equilibrate the sample to room temperature.
2 Remove the custody seal if present and place the vial in the appropriate position of the autosampler.
3 For MS/MSD sample inject the specified amount of the standard through the septum and place the vial in the autosampler.

APPENDIX E.
RECOMMENDED INSTRUMENT PARAMETERS

RECOMMENDED GC/MSD PARAMETERS

MSD Parameters

The operating parameters for this system are listed below. Actual operating conditions may vary slightly to optimize instrument

BFB analysis

PARAMETER	SETTING
Injector temperature	200°C
Column Stability time	0.5 minutes
MS Quad	150°C
MS Source	230°C
Initial Oven Temp	100°C
Initial Oven Time	0.5 minutes
Temperature Ramp	25°C/minute for 3.6 minutes
Final Oven Temp	190°C
Final Hold Time	1.5 minutes
Inlet mode:	Split
Split vent flow:	2 mL/min
Column Flow rate	0.97 mL/min at constant flow mode
Electron Energy	70 volts (nominal)
MS Scan range	35-260 amu

VOA analysis

PARAMETER	SETTING
Injector temperature	200°C
Column Stability time	0.25 minutes
Column Flow rate	0.92 mL/min at constant flow mode.
Initial Oven Temp	35°C
Initial Oven Time	4.0 minutes
Temperature Ramp	8°C/minute to 180°C for 0 minutes; 25°C/minute to 220°C
Final Oven Temp	220°C
Final Hold Time	7.0 minutes
Inlet mode:	Split, Split Ratio 2:1
Split flow:	2 mL/min.
MS Quad	150°C
MS Source	230°C
Electron Energy	70 volts (nominal)
MS Scan	SIM Mode
Ions	61, 75, 79, 95, 107, 109, 110, 114, 155, 157, 174, 176
Dwell time	100 for each ion

Analytical system preparation:

Leak Checking
From the ChemStation Instrument Control panel of the Agilent 5975C MSD select View, Tune and Vacuum control.
Select Spectrum scan. Check the nitrogen (m/z 28), water (m/z 18), to FC43 (m/z 69) ratio. Ratios for ions 28 and 18 should not exceed 20% of ion 69. Values higher than indicated above are indicative of large leaks and must be corrected.

Auto Tuning
Perform an autotune of the analytical system prior to an initial calibration, whenever the mass spectrometer is shut down, or the source is cleaned.

Perfluorotributylamine (FC43) is the compound used to perform the mass calibration of the instrument. Proper tuning of the instrument is necessary to produce standardized fragmentation patterns of target and non-target compounds.

The autotune software will adjust the mass ratio, abundance, peak shape, width, isotope peak resolution, and mass assignment.

An autotune report will be generated and the parameters will be saved in ATUNE.U.

Preparation for an Initial Calibration
Perform an autotune of the analytical system prior to an initial calibration.

1. The system should be reset to default parameters as follow:
   a. From the ChemStation Instrument Control panel of the MSD select View, Tune and Vacuum control. Select File, Reset to Default, Autotune.
   b. If the DC polarity for the system is normally set to negative for the system, resetting the tune parameter will set it to positive. Set the parameter to negative by selecting Parameters, Manual tune, DC polarity and slide the polarity selector to negative.
2. Save the default parameters by selecting save tune, Autotune.u.
3. Autotune the system by selecting Tune, Autotune.
4. The system will generate an Autotune report.
5. Save the resulting tune file by selecting File, Save tune Value
6. The tune file name is selected as outlined in the "ChemStation File Naming Convention".
7. Generate the tuning report by selecting File, Generate report.

Preparation for a Continuing Calibration

1. Perform a mass axis calibration of the analytical system prior to continuing calibration. By selecting calibrate, Mass axis.
2. Save the resulting tune file by selecting File, Save tune Value.
3. The tune file name is selected as outlined in the "ChemStation File Naming Convention".
4. Generate the tuning report by selecting File, Generate report.

Manual tuning

If the system fails to meet the tuning criteria, the source may need to be cleaned or manual tuning may be required. BFB or DFTPP tuning routines may be used to correct ions ratios.

To manually tune the system, select Manual Tune from View menu in Instrument Control view and manually tune the MSD, using ATUNE.U as reference. Adjust the parameters of Ion Focus, Entrance Lens, Repeller, Entrance Lens Offset, EM voltage etc to suit your analysis needs.

Incorporate the new tune parameters and generate today's method

1. Load a copy of the last initial calibration from C:\HPCHEM\1\Methods\Initial.
2. From the ChemStation Instrument Control panel of the Agilent 5975C MSD click on Select MS Tune File icon, click on the name of tune file generated today.
3. Select MS/SIM San Parameters. If necessary, adjust the EM voltage by adding or subtracting voltage relative "REL" to today's tune voltage.
4. Save the resulting method file as outlined in the as outlined in the "ChemStation File Naming Convention" by selecting File, Save method.

Mass Calibration

Perform mass calibration of the analytical system prior to an initial calibration, whenever the mass spectrometer is shut down, or whenever there is a mass miss-assignment is noted. Mass calibration is performed to ensure the accurate assignment of masses to ions generated in the ion volume of the mass spectrometer.

APPENDIX F.
PREVENTATIVE MAINTENANCE REQUIREMENTS

Item	Frequency	Actions/Comments
Split vent trap	As Needed	Replace.
Syringes and/or syringe needles	As Needed	Replace syringe if dirt is noticeable in the syringe, if it cannot be cleaned, if the plunger doesn't slide easily, or if clogged. Replace needle if septa wear is abnormal or the needle becomes clogged.
Inlet liner	With each ICAL	Check often. Replace when dirt is visible in the liner or if chromatography is degraded.
Liner O-rings	With each ICAL	Replace with liner or with signs of wear.
Inlet septum	With each ICAL	Check often. Replace when signs of deterioration are visible (gaping holes, fragments in inlet liner, poor chromatography, low column pressure, etc.).
Inlet Hardware	Annually	Check for leaks and clean. Check parts and replace when parts are worn, scratched, or broken.
Column Maintenance	As needed	Remove 1/2-1 meter from the front of the column when experiencing chromatographic problems (peak tailing, decreased sensitivity, retention time changes, etc.).
Column Replacement	Annually or as needed	When trimming no longer returns chromatographic performance.
Ferrules	As needed	Replace ferrules when changing columns and inlet/detector parts.
Purge/Sample Lines	Annually or as needed	Bake out and purge. Clean with organic free water if necessary.
Trap	Every 6 months or as needed	Replace with loss of performance/low response.

MS Maintenance

Task	Every Week	Every 6 Months	Every Year	As Needed
Tune the MSD				✓
Check the foreline pump oil level	✓			
Check FC43 level		✓		
Replace the foreline pump oil		✓		
Clean the ion source				✓
Check the carrier gas traps on the GC				✓
Replace worn out parts				✓
Lubricate sideplate or vent valve O-rings				✓

APPENDIX G.
CHEMSTATION FILENAMING CONVENTIONS

Files for data, methods, tunes, and sequences on ChemStation computers and the LAN are named using the following naming conventions:

Directories

On the Workstation (When available, use D: drive):

Data:	C:\MSDCHEM \1\DATA\YEAR\DATA\MMDDYYSS or D:\MSDCHEM\YEAR\DATA\MMDDYYSS
Methods:	C:\MSDCHEM\1\DATA\YEAR\METHODS or D:\MSDCHEM\YEAR\METHODS
Sequences:	C:\MSDCHEM\1\DATA\YEAR\SEQUENCE or D:\MSDCHEM\YEAR\SEQUENCE
Tunes:	C:\MSDCHEM\1\5973N or C:\MSDCHEM\1\5975

On the LAN:

Data:	I:\DATA\ROOM NUMBER\INSTRUMENT\YEAR\DATA\MMDDYYSS
Methods:	I:\DATA\ROOM NUMBER\INSTRUMENT\YEAR\METHODS
Sequences:	I:\ DATA\ROOM NUMBER\INSTRUMENT\YEAR\SEQUENCE
Tunes:	I:\ DATA\ROOM NUMBER\INSTRUMENT\YEAR\TUNE

Methods
MMDDYYATC

Sequence
MMDDYYCSS

Data Files
MMDDYYCSS

Tune Files
MMDDYYA

Variables

A: Enter analysis, as follow:

504	EDB
TO15	TO15
BNA	BNA
BNA (SIM)	PAH or PCP
PEST	PEST
PCB	PCB
RSK175	RSK
TPH-G	GRO
TPH-D	DRO
VOA	VOA
BFB	BFB

DFTPP DFT

C: Channel (use when applicable):
Front A
Back B
Both AB

DD: Day i.e. 01, 02, 03, ….

MM: Month i.e. 01, 02, 03, ….

SS: Sequential number 01, 02, 03, ….

T: Matrix Type (if applicable)
Water W
Solid S
Air A
Oil O
Other X

YY: Year i.e. 13 for 2013

APPENDIX H.
REVISION HISTORY

STANDARD OPERATING PROCEDURE: 353
Revision: 3, Effective: 10/17/2016

Low Level Volatiles

Revision	Effective Date	Description
0	10/31/2008	1. New SOP.
1	06/06/2011	1. Changed internal standard and surrogate to 1,2,3-trichloropropane-d5 and bromofluorobenzene, respectively. 2. Updated target analyte list to include 1,2,3-trichloropropane, 1,2-dibromoethane (EDB), and 1,2-dibromo-3-chloropropane (DBCP) and remove 1,2-dichloropropane. 3. Added provision for alternative analytical systems. 4. Minor edits throughout. 5. Appendix F, updated maintenance schedule.
2	08/05/2013	1. Combined CCV and LCS into one analysis. 2. Updated sections 3 and 11 to current format. 3. Minor edits throughout for clarity.
3	10/17/2016	Limited revision to address the following: 1. Removed preparation of standards in 50-mL syringe in Section 8.3.2 and Appendix D. 2. Corrected volumetric flask size for BFB solution in Section 7.3.2. 3. Removed typical data package format (Appendix H). 4. Updated control limits for BS/MS/Surrogate and method performance data. 5. Minor edits throughout.